METHODS FOR REDUCING VOLATILE ORGANIC CONTENT IN FABRIC WATERPROOF COATINGS

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Fabrics for rainwear and outdoor equipment traditionally have been rendered waterproof by coating with solventborne rubber solutions, solventborne polyurethanes and vinyl plastisols. Regulatory pressure for environmental protection and worker safety has become a potent driving force in eliminating volatile organic solvents and toxic additives from commercial coating products. A variety of low-solvent coating technologies are being introduced to replace the traditional solvent-based products. These include high solids formulation, solventless UV and electron beam curing systems, powder coatings and supercritical CO_2-reduced paints. The benefits and limitations of these coating technologies were compared with respect to their applicability to fabric waterproofing. In addition, a novel acrylated surfactant was synthesized and employed in the formulation of UV-curing waterborne coatings for textile waterproofing. The application methods and cure characteristics of the solvent-free formulations are described. Physical properties of cured coating films including tensile strength, percent elongation, water absorption, water drop contact angle, and adhesion to common fabrics were measured and compared to those obtained using a commercial waterborne waterproofing system. One formulation produced cured films having low water absorption, tenacious adhesion to polyester fabric and surface hydrophobicity properties approaching those of polyethylene.

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TABLE OF CONTENTS

CONTENTS (Continued)

CONTENTS (Continued)

LIST OF FIGURES

LIST OF TABLES

EXECUTIVE SUMMARY

Fabrics for rain gear and outdoor equipment traditionally have been rendered waterproof by coating with solventborne rubber solutions, solventborne polyurethanes and vinyl plastisols. Regulatory pressure for environmental protection and worker safety compliance have become potent driving forces in eliminating volatile organic solvents and toxic additives from commercial coating products. A variety of low-solvent coating technologies are being introduced to replace the traditional solvent-based products. These include high solids formulation, solventless UV and electron beam curing systems, powder coatings and supercritical carbon dioxide-reduced paints. The benefits and limitations of these coating technologies were compared and contrasted with respect to their applicability to fabric waterproofing.

The experimental portion of this research addressed the feasibility of developing new coating materials and application processes for effectively rendering fabrics water-repellent by safe industrial practices with minimal environmental impact. This application requires coating materials which are easily applied, shelf stable, compatible with common clothing fabrics, and have outstanding water repellency and durability. Preliminary results suggest that waterproofing agents delivered from either aqueous vehicles or in the absence of diluents will be the best approach to achieving the necessary product performance while minimizing organic solvent emissions.

To prepare this new class of water-reducible UV light-curing textile waterproofing agents, a novel acrylated surfactant was synthesized and employed in the formulation of experimental coatings. The best combination of these new surfactants and traditional surfactants was determined for emulsifying a high performance commercial acrylated polyurethane. Several waterborne coating formulations were prepared from emulsified acrylated polyurethane oligomers, acrylic crosslinkers, silicone additives and photoinitiators and cured into free films for physical property testing. The cured coatings were screened for hydrophobicity by measuring water contact angle, water resistance by absorption determination, and strength by tensile testing. Selected formulations were applied to polyester fabric and the resulting coatings tested for water repellency and coating-to-fabric adhesion. The results were compared to those obtained with commercial waterborne silicone-based fabric coatings.

The mechanical and water resistance properties of coating films derived from a volatile organic content (VOC)-free ultraviolet light (UV) light curing formulation ranged from free-film tensile strengths of 200-700 psi with 7-15 % ultimate elongation, initial water drop contact angles between 90° and 30°, water absorption values of between 0.2 percent and 6 percent, and coating to fabric adhesion of up to 500 psi. The water resistance properties, in particular, appeared to be related to the total level of emulsifiers in the formulations. The polysiloxane resin content also appeared to be important in terms of surface hydrophobicity and coating flexibility.

A review of current organic solvent reducing-coating technology with potential applications in fabric waterproofing revealed that UV-curing and water-reducible formulation remain the best alternatives to current solvent-based coating methods. Recommendations for additional research in the area of UV-curing waterborne coatings would include a systematic developmental study for optimizing the waterborne UV-curing fabric coatings, investigating supercritical carbon dioxide (CO_2) as a formulation diluent for UV-curing coating applications, studying other structure-property relationships relevant to waterproof wearing apparel such as water vapor permeability, colorability, resistance to other contaminants, durability and weatherability. Addressing manufacturing issues such as material costs, labor costs, equipment requirements and worker safety would also be recommended to improve the chances for economic viability.

1

METHODS FOR REDUCING VOLATILE ORGANIC CONTENT IN FABRIC WATERPROOFING COATINGS

1.0 INTRODUCTION

Waterproof finishes are those that coat or seal a fabric so that water does not pass through it. Such fabrics are nonpermeable to air, and thus, are not comfortable in wearing apparel. Water-repellent finishes, such as ScotchgardR, result in a fabric that resists wetting and is relatively porous. These latter type of finishes are popular in consumer goods, because the fabrics are comfortable and the finish does not alter the original appearance.[1]

Early waterproofing methods involved coating the fabric with rubber, oxidized oil or varnish. These coating vehicles were all delivered from organic solvents. Rubbers and plastics are still used in the manufacture of rainwear. Porometric polyurethane coatings have been widely used as imitation leather for clothing, furniture and automobile interiors.[2] These elastomeric resins are frequently delivered as two-component solutions in organic diluents. Vinyl plastisols are another staple of the rainwear industry. They typically consist of poly(vinyl chloride) dispersions in organic plasticizers. The latter compounds are not solvents in the sense of paint thinners, which readily evaporate as the paint dries. Plasticizers must remain within the plastic to keep it soft and pliable. Environmental pollution regulations, however, have changed the way plastisols are employed. For example, the use of 2-ethylhexyl phthalate, a common vinyl plasticizer, has been curtailed because of its volatility and hazard in the workplace.[2]

It is virtually impossible to hermetically seal a surface from water vapor by using polymeric coatings alone. Polytetrafluoroethylene and polyvinylidine chloride are the best barriers with a water vapor transmission rate (WVTR) of 4.8 $(g)/(ml)/m^2(24\ hr)$. An important point about moisture resistance is that water vapor and liquid water behave very differently. Silicones are touted as being good waterproofing materials for brick, masonry, textiles, leather, etc. They do, however, have a very high WVTR. Any water droplets that collect on the silicone-coated surface will bridge over the pores rather than wicking into them.[3] This property has broad implications for the proposed waterproofing approach.

Due to the increasingly restrictive rules of the U.S. Environmental Protection Agency (EPA) regulating the amounts and kinds of solvents allowed, there has been a tremendous surge of interest in the area of low volatile organic content (VOC) coatings. It is expected that by 1995, the U. S. market for more environmentally acceptable coatings will grow rapidly, while the market for certain coatings like low-solids and high-solvent systems will fall from 44% to 26%.[4] In addition, the commercially important waterproofing coatings which depend on dilution with relatively nonvolatile plasticizers may face restrictions due to Occupational Health and Safety Act (OSHA) rules governing hazardous materials in the workplace.

This research addresses the technical feasibility of developing new coating materials and application processes for effectively rendering fabrics water-repellent by safe industrial practices with minimal environmental impact. This application requires coating materials which are easily applied, shelf stable, compatible with common clothing fabrics, and have outstanding water repellency and durability. Waterproofing agents delivered from either aqueous vehicles was one approach investigated for achieving the necessary product performance while minimizing product VOC.

1.1 Technical Objective

The major thrust of this research was to identify promising low-VOC coating technologies which could be implemented by the US. Army for waterproof clothing and fabric articles. Another facet of the research was to demonstrate through a series of laboratory experiments the feasibility of developing a waterborne UV-curing coating based on a novel acrylic-functional silicone copolymer. The proposed approach was aimed at identifying an organic solvent-free coating process that yielded coatings whose properties meet or exceed those attained for waterproof coatings delivered from conventional organic solvents.

1.2 Technical Approach

In order to achieve the desired level of viscosity reduction, emulsion stability, and cured films with excellent water resistance, UV-curable, nonionic surfactants were proposed. The different chemical constituents of this experimental coating binder were chosen so that stable water dispersions of acrylated polyurethane oligomers and polysiloxane flexibilizers would be possible and cured films would show outstanding adhesion to fabric substrates, durability, and water repellency equivalent to conventional solvent-based treatments. The unique structure of the acrylated silicone copolymer surfactants was designed to impart water compatibility when uncured and dispersed in a water base and hydrophobicity and effective barrier properties when cured to a film. The key to this behavior is the dual role of the silicone-polyether segments.

Polyethylene oxide-polydimethylsiloxane portions of the copolymer-based surfactant have outstanding emulsifying properties. In the uncured state, hydrophilic polyethylene oxide (PEO) segments should orient themselves toward the aqueous dispersion medium thus aiding the stability of the paint. Upon drying, the hydrophilic PEO portions would tend to associate with the polar substrate while the strongly hydrophobic polysiloxanes would migrate to the coating-air interface. Crosslinking the system by UV initiation would lock the copolymers in this desired orientation. The migration of low energy groups such as siloxanes to the surface of thermosetting plastics has been observed in many different systems.[5] With this morphology, the coating would exhibit maximum adhesion and water resistance. An illustration of this coating concept is shown in Figure 1.

Freshly Applied Waterborne Waterproofing Coating   Waterproof Coating After Drying and Curing

|		
Urethane-Acrylate rich region		Silicone rich region
Mercaptide rich region		Acrylic crosslinker
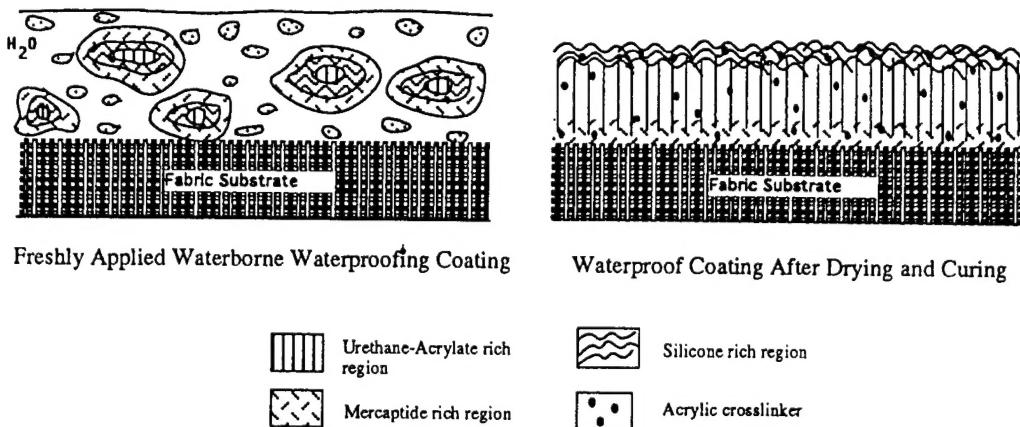
Figure 1.0   Illustration of Phase Separation in Silicone-Modified Waterborne Coatings

3

2.0 SURVEY OF LOW VOLATILE ORGANIC CONTENT COATINGS TECHNOLOGY LITERATURE

A survey of literature and commercial product information pertaining to fabric coatings with low VOC was performed to identify the most promising existing technologies. The search concentrated on the four leading low-VOC coating technologies which are waterborne, high solids, powder, and radiation cure. The different methods were compared and contrasted in terms of cost, ease of application, regulatory aspects, and general compatibility with the problem of waterproofing fabrics on a large commercial scale. The technologies investigated in the survey are described in detail in the following sections.

2.1 Waterborne Coatings and Fabric Treatments

There are many advantages associated with the use of waterborne coatings. Much of the same equipment that is used to prepare and apply conventional coatings can be used for waterborne coatings. Using water makes cleanup much easier, relieves much of the odor problem that accompanies the use of large quantities of organic solvents, decreases the fire hazard, and reduces solvent emissions. As with the other low-VOC coating technologies, there are several disadvantages such as increased drying times due to the lower volatility of water compared to organic solvents (but the surface can be smoother upon drying), poor solvent and flow characteristics, poor freeze/thaw stability, limited shelf stability, and poor detergent resistance.[6] In addition, for some systems, strict humidity control during application and pretreatments of the substrate surface are often needed.

Waterborne coatings encompass a broad area of materials and application techniques. Examples include self-crosslinking silicone emulsions, one- and two-component polyurethane dispersions, acrylic latex, and synthetic rubber emulsions. The majority of waterborne coating systems are not VOC-free, but employ varying amounts of organic solvents as coupling agents to improve resin dispersion and as coalescing aids to provide uniform film formation.[7] Low-boiling cosolvents can also increase the rate of evaporation, thus shortening drying times. One of the main problems associated with waterborne coatings is that , under conditions of high humidity, the cosolvent can evaporate before the water, often resulting in poor film formation.[8] Careful choice of cosolvents and cosolvent levels is therefore critical in waterborne coating applications. The most applicable waterborne resin types for fabric waterproofing and water repellency would be the silicone emulsions, polyurethane emulsions and fluoropolymer dispersions. Common latex polymers such as vinyl acetate, acrylic, and styrene-acrylic typically dry to hard rigid films and thus would not be suitable for fabric coating. Elastomer latexes such as styrene-butadiene rubber (SBR) which are frequently used in construction adhesives usually dry to tacky materials. High temperature vulcanization is normally used to achieve tack-free coatings. Currently available waterborne resins which possess some of the desired properties of flexibility, hydrophobicity and relatively low temperature processing requirements are the silicone, fluoropolymer, and polyurethane dispersions. These materials are described in more detail in the following sections.

<u>Silicone Emulsions</u>

Dow Corning Corp., GE Silicones and Wacker Silicones Corp. market impregnating emulsion products for treating fabrics. Dow Corning's Fabric Coating 61 is a one-component, anionically stabilized, water-based elastomer which cures at room temperature to a protective, water-resistant coating.[9] This product was evaluated both alone and as an additive to the proposed UV curing acrylic waterproofing coatings. The Wacker emulsion product offers similar properties but is sold as a concentrate that must be emulsified and quickly applied. The concentrate product, S-Finish WS-63 M, is a blend of methylhydrosilyl-functional silicone fluids and can evolve hydrogen gas upon prolonged storage after emulsification.[10]

4

Fluoropolymer Dispersions

Durable oil- and water-repellent finishes for fabrics based on proprietary dispersions of fluoropolymers in water are available commercially from a number of sources including ICI, LTD. and E.I DuPont De Nemours & Co. One such product is the Milease[R] line from ICI Specialty Chemicals. These fluoropolymer emulsions are typically blended with waterborne thermosetting resins such as melamine-formaldehyde condensates and applied to fabrics by spray or dipping. The finishes are dried and cured at elevated temperatures (179-180 °C) for several minutes and are reported to render a variety of natural and synthetic fabrics effectively water- and oil-resistant. These systems have also been approved for use in Quarpel water- and oil-repellent treatments for military fabrics.[11] DuPont's Zepel is composed of a series of fluoroalkyl-substituted acrylates and methacrylates. This material can be emulsified and blended with waterborne thermosetting resins to yield oil- and water-repellent fabric finishes. Canadian researchers have modified Zepel with fluoroalkyl-subtituted silanes and polysiloxanes to achieve fabric finishes with higher levels of oil and water repellency.[12] While these water-repellent products are not true waterproofing agents, the inclusion of film-forming polymers such as polysiloxanes was found to improve oil and water resistance and could theoretically be used to waterproof fabrics if applied in thicker layers.

Polyurethane Dispersions

Aqueous polyurethane dispersions have been developed as resin binders and resin additives for low-VOC wood coatings and industrial maintenance coatings. Although most commercial polyurethane-based coatings are formulated for high hardness and toughness, the polyurethane class is versatile enough to allow for waterborne elastomeric coatings as well. These materials are most frequently encountered in adhesive applications. The preparation of polyurethane dispersions can be accomplished in several ways. The procedure claimed at present to yield the highest quality products involves the reaction of isocyanate-terminated prepolymerizing a water-miscible solvent such as acetone, with a diamine carboxylate or sulfonate. The resulting polyurethane ionomer solution is mixed with water which forms a dispersion and chain-extends the polymer. The organic solvent can then be removed under reduced pressure and recycled.[13] Other polyurethane dispersion methods include emulsification of high molecular weight thermoplastic polyurethanes and surfactants dissolved in organic solvents followed by solvent removal and emulsifying blocked-isocyanate-terminated urethane oligomers with suitable crosslinkers in water.

Commercial suppliers of flexible polyurethane dispersions for adhesive applications include: BASF Wyandotte, Inc.; Dainippon Ink and Chemicals, Inc.(Vondic 1000 series); Verona Div. of Bayer, A.G. (Impranil 4496); Refined Onyx Division of Millmaster Onyx Corporation (Karathane 5A and 5HS); and the Nopco Chemical Division of Diamond Shamrock Corporation.[13]

2.2 High Solids Coatings

High solids coatings employ lower molecular weight polymer resins than conventional solventborne coatings in order to reduce application viscosity without excessive volatile organic solvent dilution. Using high molecular weight polymers such as those found in acrylic lacquers produces highly viscous materials with poor application characteristics. Therefore, the molecular weight (and thus the viscosity) of the resins must be reduced to compensate for the reduction in solvent. In addition, the resins used in high solids formulations should have functional groups which will react in a post-curing step to produce higher molecular weight networks with improved mechanical properties. High solids formulation can be thought of as a compromise between the easy-to-apply thermoplastic lacquers and thermosetting systems such as epoxies. They are typically formulated to possess serviceable application properties while remaining below government-mandated VOC content. This requires a careful balance of binder resin molecular

weight, polymer reactive functionality, pigmentation and flow control additives to achieve desired application characteristics and coating performance. Some of the drawbacks associated with the high solids formulation approach include: higher than average application viscosities, which can cause difficulty in applying thin films; shorter potlife; and anticipated regulatory pressure to reduce or eliminate organic solvents completely. The latter limitation may be particularly important in fabric treatments which often require thin coatings.

The combination of high solids and waterborne formulation has been successfully used for polyurethane-based maintenance coatings.[14] Coatings employing a novel urethane diol as a modifier for high solids acrylic emulsions were prepared. When the urethane diol was used as a cosolvent, it was possible to formulate high solids waterborne coatings without additional VOC-contributing solvents or preneutralization with amines.

2.3   Powder Coatings

Powder coatings are based on thermoplastic and thermosetting polymer resins which are applied as dry powers and thermally cured to coherent films. This rapidly growing technology offers several practical and environmental advantages including low volatiles emissions, excellent film-forming properties, and low-waste generation. The dry powder particles are frequently applied by fluidized bed and electrostatic spray techniques.[15] The latter method has been found to produce thinner finished coatings than the fluidized bed technique.[15, 16] Epoxy-based powder coatings currently have the highest share (up to 90%) of the powder coatings market. Epoxy-based coatings tend to be hard and brittle which generally would preclude their use on clothing articles. Fairly high curing temperatures are required to melt and cure powder coatings which may be deleterious to some fabrics. Assuming theoretically that highly flexible waterproof coatings could be applied from powder precursors, there would be still be other economic- and performance-related hurdles to overcome. Since powder coatings are applied by a radically different process than conventional textile coatings, large capital expenditures for specialized equipment would be required to implement this technology. Another limitation of powder coatings is the difficulty in obtaining thin films over complex substrates.

2.4   Radiation Curing

In recent years there has been considerable interest in the preparation, properties and applications of radiation cure coatings. This versatile class of materials includes the well known decorative coatings used on aluminum beverage cans and interior wood paneling products as well as emerging high-performance adhesives and coatings products. The benefits of radiation curing are manifold. This approach allows rapid processing and nearly solventless formulations in some cases. Radiation curing compositions are particularly well suited to the deposition of thin films over thermally-sensitive substrates. The rapid cure speeds possible with these systems make them excellent candidates for the continuous reel-to-reel manufacturing processes used in the textile industry.

UV Curing

UV radiation in the spectral range of 300-430 nm and organic photoinitiators are used to crosslink acrylate-functional resins. The medium pressure mercury arc lamp offers the maximum output within this preferred range. These lamps, which are commercially available at intensities of 100-300 watts per linear inch, can effectively cure coatings of up to 10 mils in thickness. Substrates coated with UV-curing coatings are typically processed by means of a conveyor line passing below a bank of UV lamps. This arrangement can be easily integrated into a variety of commercial fabric-finishing processes. One of the drawbacks of UV curing is that oxygen interferes with surface

curing by forming oxyplex radicals. Blanketing the coated surface with an inert gas or using higher levels of photoinitiators are ways of circumventing oxygen cure inhibition. [17]

The supercritical fluid spray process is a recent innovation in coating deposition technology. The process uses supercritical carbon dioxide (CO_2) to replace volatile organic solvents in conventional and high solids coating formulations. The technology has been found to be particularly effective in replacing high-flash solvents such as methylethyl ketone (MEK) and chlorinated hydrocarbons, while actually improving the surface appearance and performance of spray-applied coatings.[7] Supercritical CO_2 assisted spray can be used with a variety of different polymer systems including waterborne and UV light-cured coatings. The latter is particularly intriguing since a process could be envisioned where a UV-curing coating is applied by supercritical CO_2 assisted spray and cured as the CO_2 gas evolves from the coating, thus blanketing the substrate and preventing oxygen cure inhibition.

EB Curing

Electron-beam (EB) curing differs from UV curing in that the source of radiation for the former is a directed beam or curtain of highly accelerated electrons which are injected into the coating. This more highly energetic curing technique allows coating formulation without photoinitiators. Electron beam curing systems also allow curing of thicker and more highly pigmented coatings and do not suffer from oxygen inhibition as UV curing systems do.[18] Despite these obvious advantages over UV light initiation, EB curing is not as widely used. This stems from higher equipment costs and increased hazards of using more energetic radiation sources.

2.5 Thermal and Moisture Curing

In addition to radiation curing, polymeric fabric coatings can be cured by thermal means and by absorbing environmental moisture. Thermally-cured coatings are rather ubiquitous in that practically all coating application methods involve heating in some way. Moisture-curing polymers are more frequently encountered in adhesives but can, in principle, be used for waterproof fabric coatings. These curing methods are described in the following sections.

Thermal Curing

Most coatings require heat treatment at some point in their application process. Thermal energy is used reduce to the viscosity of plastisols, to remove solvents or water from freshly coated substrates, to accelerate the curing reactions of thermoset polymers such as two-pack polyurethanes, and to consolidate or sinter dispersed polymer particles such as poly (vinyl chloride) in plastisols or epoxy-based powder coatings. Heating systems that are frequently used in fabric coating operations include: convection ovens, cylindrical heating units, and radiation (infrared) ovens.[2]

Moisture Curing

Moisture curing has been successfully employed in polyurethane- and epoxy resin-based coatings as well as with silicone sealants. Isocyanate-terminated polyurethanes, catalyzed with tertiary amines, react with atmospheric moisture and crosslink into elastomers.[13] Carbon dioxide evolves from these systems during cure. Silicone room temperature vulcanizates (RTVs) can cure by this mechanism as well, evolving small organic molecules, e.g., acetic acid, methanol, acetone in the process. Problems associated with moisture-curing systems include: dependence on ambient relative humidity, gradient curing from outside to inside the coating, porosity due to gas evolution, and generally slow cure rates.

2.6 Fabric-Coating Equipment

The types of fabric-coating equipment required for applying UV curing compositions already exists and need only be augmented for the UV irradiation step. Manufacturing line designs which will be considered for this application include: multiple head spread coaters, spray coaters, and roll coaters. Infrared (IR) ovens for rapid water flash-off could also be incorporated into the system before the UV irradiation and final take-up.

3.0   EXPERIMENTAL

The experimental portion of this program involved: the synthesis of novel acrylated poly (siloxane-co-ethylene oxide) surfactants; an emulsification study to identify a surfactant or surfactant blend which could effectively disperse the polymeric constituents of the coatings in water; curing waterborne coatings by UV light initiation, and measuring the physical properties of the resulting materials. The experimental methods used to synthesize the novel surfactants and formulate UV-curing waterborne fabric coatings are described in the following sections.

3.1   Preparation of Acrylated Poly(dimethylsiloxane-co-ethylene oxide) Copolymers

Synthetic Procedure

The acrylic ester endcapping reaction was carried out by reacting carbinol-terminated siloxane copolymers with acryloyl chloride in the presence of a solid heterogeneous acid acceptor. The derivatizations were performed in dry toluene solution using crosslinked poly(vinyl pyridine) beads to scavenge the liberated HCL. A slight stoichiometric excess of the acryloyl chloride was used to ensure complete reaction of the copolymer endgroups. The derivatization reactions were monitored by Fourier Transform Infrared Spectroscopy (FTIR). Representative FTIR spectra are provided in Appendix A. The carbinol-terminated copolymers were first characterized by reacting weighed amounts with an excess of acetic anhydride in the presence of pyridine, hydrolyzing the remaining acetic anhydride with water and titrating the acid with a standardized NaOH solution. A blank was run using the same volume of acetic anhydride without the carbinol compound. Comparisons with the titrated blank samples allow calculation of the total carbinol groups in the sample and, thus, the molecular weight of the copolymers. A typical derivatization procedure is described in Appendix B.

Viscosity Characterization

The average viscosity of the products was measured at room temperature using a Brookfield rotary viscometer model LVT with small sample adapter and spindle #16. The viscosity obtained at several different shear rates was 520 ± 30 cps. For the PS 556-derived material, the fluid rheology appeared to be Newtonian, i.e., the measured viscosity appeared independent of the applied shear rate.

The acrylated PS 555 material was prepared by an analogous procedure with the exception that no gellation was observed upon vacuum stripping. The average viscosity obtained at several different shear rates was 560 ± 80 cps. The rheology of this material appeared to be slightly dilatent in nature, i.e. the measured viscosity increased with increasing shear rate.

3.2   Coating Formulation and Water Dispersability Study

3.2.1 Preliminary Screening of UV Curing Coatings

Preliminary coating formulations were prepared by dissolving together acrylated oligomers, crosslinkers, photoinitiators and other additives. The formulations were poured into aluminum sample pans, allowed to dry and were irradiated for 1-2 minutes under a blanket of carbon dioxide gas. The light radiation source was a 300 W, high intensity, deep UV Xenon lamp (Model 66178, Oriel Corp., Stamford, CT). The properties of film strength, flexibility, color and water repellency were determined to screen the various formulations. These experiments were performed without

water dilution to determine first whether the final cured material properties warranted further examination as waterborne systems. The materials and emulsifiers proposed and partially evaluated are listed in the following section.

The results of the initial qualitative screening study indicated that the RSX 89462 oligomer, when formulated with TMPTA or TRPGDA crosslinkers, Irgacure 907 or benzoin methyl ether initiator, and either of the acrylated PS-PEODA fluids or mercapto-functional polysiloxane gave the best UV cure response, cured film properties and low color. The Genomer D1200PD, an ester-based polyurethane acrylate also gave excellent cured film properties. The oligomer, however, was found to be very difficult to disperse in water and its use in this program was discontinued. The Ebacryl 6700 was also found to be difficult to disperse and is very high in viscosity. The Ebacryl 230 appears water dispersible but produces cured films with very low tensile strength. The majority of the formulation effort therefore focused on the RSX 89462.

3.2.2 Emulsification of RSX-89462-Based UV Curing Formulations

Acrylic waterproofing coatings were typically formulated by first dissolving together the PS-PEODA, TMPTA, mercaptyl-substituted polysiloxane, acrylated oligomers and photoinitiators in PGMEA and then mixing in water to form an emulsion. A study was conducted to determine the best combination of emulsifying agents to use for dispersing the acrylated polyurethane RSX 89462 with water and the other materials necessary for curing the coating. A variety of surfactants were evaluated including the acrylated poly (siloxane-co-ethylene oxide) oligomers, commercial non-ionics, and commercial anionics. The non-ionic and anionic types are listed in Table 3.1. Each sample was mixed for a 5-minute period at 5000-6000 RPM by means of a high-speed disperser (Model CM-100, D. H. Melton Co.). The degree of emulsion stability and other formulation characteristics were noted. The compositions tested in this RSX 89462 emulsifying study are listed in Table 3.1.

Table 3.1
Surfactants

Surfactant	Chemical Name	Emulsifier Type	Source
PS-PEODA-50	Acrylated PS 555	non-ionic	Cape Cod Research
PS-PEODA-76	Acrylated PS 556	non-ionic	Cape Cod Research
Hamposyl L-95	Sodium lauroyl sarcosinate	anionic	W. R. Grace & Co.
Hamposyl O	Oleoyl sarcosine	non-ionic	W. R. Grace & Co.
Surfynol 104E	Tertiary acetylenic diol	non-ionic	Air Products, Inc.
Span 80	Sorbitan monooleate	non-ionic	ICI Chemicals
Brij-30	Polyoxyethylene(4) lauryl ether	non-ionic	Aldrich Chemicals
Desonic 9N	Nonyl phenol polyethoxylate	non-ionic	Witco Chemicals

10

Table 3.2
RSX 89462 Emulsification Study Formulations

RSX 89462-S$_a$1

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	5.534	90.84	44.65
TMPTA	0.286	4.69	2.31
Surfactant	0.105	1.72	0.85
Irgacure 907	0.167	2.74	1.35
PGME	0.314	------	2.53
Water	5.987	------	48.31

RSX 89462-S$_a$2

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	5.534	89.30	44.28
TMPTA	0.286	4.62	2.29
Surfactant	0.210	3.39	1.68
Irgacure 907	0.167	2.69	1.34
PGME	0.314	------	2.51
Water	5.987	------	47.90

RSX 89462-S$_a$2, S$_b$1

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	5.534	87.81	43.91
TMPTA	0.286	4.54	2.27
Surfactant 1	0.210	3.33	1.67
Surfactant 2	0.105	1.67	0.83
Irgacure 907	0.167	2.65	1.33
PGME	0.314	------	2.49
Water	5.987	------	47.51

RSX 89462-S$_a$2, S$_b$2

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	5.534	86.37	43.55
TMPTA	0.286	4.46	2.25
Surfactant 1	0.210	3.28	1.65
Surfactant 2	0.210	3.28	1.65
Irgacure 907	0.167	2.61	1.31
PGME	0.314	------	2.47
Water	5.987	------	47.11

Formulation Properties

The properties of coating formulations prepared from the novel acrylic copolymers were studied. The effects of resin loadings and additives on viscosity and dispersion stability were determined. A Brookfield Model LVT viscometer was used to measure formulation viscosities. The viscosities were measured at different spindle RPMs to measure any formulation thixotropy or other departure from Newtonian viscosity characteristics. Selected compositions were also stored in closed containers at room temperature and sampled periodically over the course of a month. The formulations were visually inspected for signs of instability. The information obtained can be used to predict the shelf life of the dispersions.

11

3.3 UV Cure Study of Waterborne Coatings

The photoinitiated cure of experimental waterborne acrylic coating compositions was studied to determine the viability of rapidly curing these materials. Initially, aqueous dispersions of acrylated silicone-polyether, urethane acrylate oligomer (RSX 89409, UCB Radcure), mercaptyl-functional silicone oligomer (PS 849 and/or PS 850.5, Huels America Corp.), acrylic crosslinker and photoinitiator were placed in 0.5 in deep aluminum foil sample, dried in an air-circulating oven maintained at 100 °C for 5-10 minutes and irradiated with UV light. Free films of the cured coatings were cut into strips and tested for ultimate tensile strength and elongation according to ASTM D 2370. From these data, a preliminary understanding of the factors governing cure rate and composition-property relationships were developed.

Two UV radiation sources were used in this study. The majority of the cure study was conducted using an Oriel Model 66178 equipped with a 300 W high-intensity, deep UV Xenon lamp (Oriel Corp., Stamford, CT). The lamp provides a UV and visible spectrum that approximates a 6000 K color temperature continuum. The lamp housing has built-in 90-degree angle fused silica reflector. Samples can be positioned 1 to 50 cm below the housing to obtain different exposure intensities. The area of irradiation was somewhat limited with this UV source. A Fusion Model F300-6 UV Curing System (Fusion Systems Corp.) having a 300 W medium pressure mercury "H" bulb source and conveyor system capable of speeds between 4-40 feet per minute was used in later experiments, and provided the best and most controllable source of UV radiation. Coating samples were typically run at a conveyor rate of 4 ft per minute. Two to four passes by the 1 in by 6 in light slit were generally used.

3.4 Fabric Coating and Physical Properties Testing

Dacron polyester and nylon fabrics were dip coated with selected coating formulations, dried and UV cured using the conditions determined in the cure study. The degree of water repellency was determined by contact angle measurements. Coating to fabric adhesion was also measured quantitatively.

Contact Angle

A Gaertner Scientific goniometer was used to measure the contact angle of water droplets on the cured free films and coated fabrics. The contact angle values were compared to those measured for fabrics coated by traditional methods with state-of-the-art silicone rubber dispersions. This commercial product was used as a control for the following reasons: it effectively seals fabric substrates with a waterproof film, it is water-based like the proposed experimental coatings and is representative of low-VOC waterproof treatments, and its high silicone resin content makes it an interesting comparison to the proposed silicone-modified polyurethane coatings.

Water Absorption

The degree of water resistance was determined by a water absorption test according to ASTM D 570. Free film samples of cured coating material were oven-dried at 100 °C, allowed to cool to ambient temperature in a desiccator and pre-weighed using a Mettler 4-place analytical balance. The dried samples were immersed in water maintained at room temperature for 2 hours, blotted with paper towel to remove excess water and reweighed. The degree of water absorption was calculated and reported as a percentage change. The effect of compositional changes on the degree of water exclusion was determined for each formulation.

Coating Adhesion

The fully cured coatings were tested for adhesion performance according to a variation of ASTM D-4541-85. Fabrics treated with experimental coating formulations were adhered to one face of a 2 " diameter aluminum cylinder having a peg protruding from the opposite face for mounting in the jaws of a universal tensile testing machine. Another aluminum cylinder having a diameter of 0.5 in was bonded to the coated surface with the same high strength epoxy adhesive. The cylinder end was held in one grip of a universal tensile testing machine and the adhered cylinder end in the other grip. The adhesion of the UV-cured coating to the fabric was determined by pulling the adhesively bonded specimen apart in a constant strain rate tensile test. A strain rate of 2 in/min was used. Coating adhesion was reported in lbs/in^2 and the mode of failure noted.

4.0 RESULTS AND DISCUSSION

4.1 UV Curable Poly(dimethylsiloxane-co-ethylene oxide) Surfactants

The acrylated poly(dimethylsiloxane-co-ethylene oxide) oligomers were prepared by esterifying carbinol-terminated poly(dimethylsiloxane-co-ethylene oxide) oligomers with acryloyl chloride. Crosslinked poly(vinyl pyridine) beads were used as a heterogeneous acid scavenger. The chemical reaction is illustrated in Figure 4.1.

$$x \ HO \text{-}(CH_2\text{-}CH_2\text{-}O)_m\text{-}R\text{-}(\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O)_n\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}R\text{-}(O\text{-}CH_2\text{-}CH_2)_m\text{-}OH \ + \ (2x+i) \ CH_2{=}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl$$

$$NR_3 \ \Big\downarrow \ \Delta$$

$$CH_2{=}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_m\text{-}R\text{-}(\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O)_n\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}R\text{-}(O\text{-}CH_2\text{-}CH_2)_m\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH{=}CH_2$$
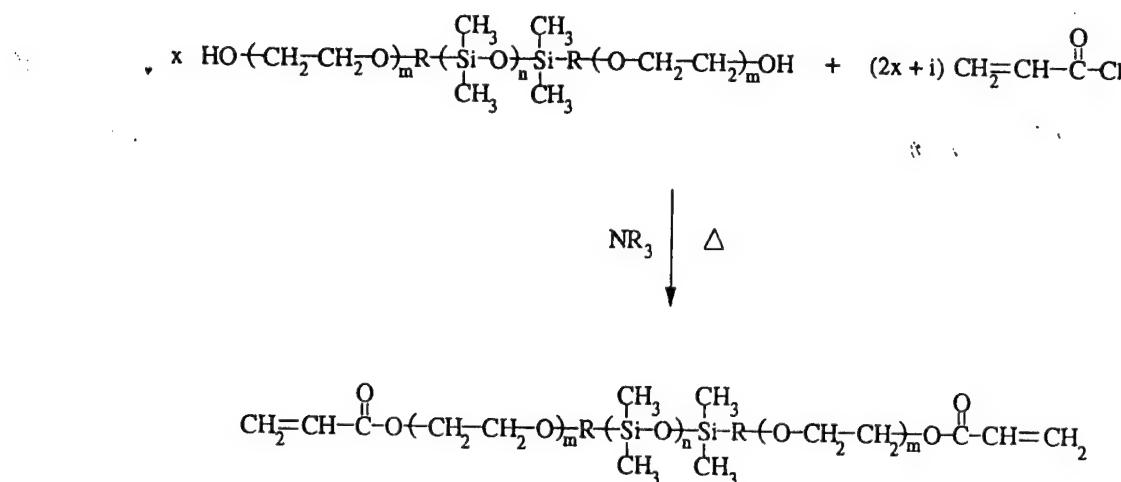
Figure 4.1   Synthesis of Acrylated Poly(dimethylsiloxane-co-ethylene oxide) Oligomers

The acrylated oligomer based on PS 555 was readily dispersible in water, yielding translucent and homogeneous mixtures. The acrylated oligomer based on PS 556 which has a higher poly(ethylene oxide) content appeared to dissolve completely in water leaving a clear solution. This latter property was found to be beneficial in developing effective surfactant systems for emulsifying commercial UV-curing coating resins.

4.2 Formulation of Waterborne UV-Curing Coatings

4.2.1 Waterborne UV-Curing Coating Emulsification Study

The results of a study conducted to determine the best combination of emulsifying agents to use for dispersing the acrylated polyurethane RSX 89462 and other essential coating components are provided in Table 4.1.

14

Table 4.1
RSX 89462 Dispersability Matrix

Surfactant 1	Surfactant 2	Surfactant 1 Level Wgt. %	Surfactant 2 Level Wgt. %	Dispersion Quality Index[1]	Comments[2]
PS-PEODA-76	----------	0.85	------	1	LF
PS-PEODA-76	----------	1.68	------	1	LF
PS-PEODA-50	----------	0.85	------	1	LF
PS-PEODA-50	----------	1.68	------	1	LF
PS-PEODA-50	PS-PEODA-76	1.67	0.83	1	MF
PS-PEODA-50	PS-PEODA-76	1.65	1.65	1	MF
Hamposyl L-95	----------	0.85	------	1	HF
Hamposyl L-95	----------	1.68	------	1	HF
Hamposyl L-95	PS-PEODA-76	1.67	0.83	1	HF
Hamposyl L-95	PS-PEODA-76	1.65	1.65	1	HF
Hamposyl O	----------	0.85	------	1	HF
Hamposyl O	----------	1.68	------	1	HF
Hamposyl O	PS-PEODA-76	1.67	0.83	1	HF
Hamposyl O	PS-PEODA-76	1.65	1.65	2	HF
Surfynol 104E	----------	0.85	------	1	HF
Surfynol 104E	----------	1.68	------	1	HF
Surfynol 104E	PS-PEODA-76	1.67	0.83	3	HF
Surfynol 104E	PS-PEODA-76	1.65	1.65	3	HF
Span 80	----------	0.85	------	1	MF
Span 80	----------	1.68	------	1	MF
Span 80	PS-PEODA-76	1.67	0.83	1	MF
Span 80	PS-PEODA-76	1.65	1.65	1	MF
Brij-30	----------	0.85	------	1	MF
Brij-30	----------	1.68	------	1	MF
Brij-30	PS-PEODA-76	1.67	0.83	1	MF
Brij-30	PS-PEODA-76	1.65	1.65	1	MF
Desonic 9N	----------	0.85	------	1	HF
Desonic 9N	----------	1.68	------	1	HF
Desonic 9N	PS-PEODA-76	1.67	0.83	3	HF
Desonic 9N	PS-PEODA-76	1.65	1.65	3	HF

1: 1 = lowest level of dispersion, 5 = highest level of dispersion
2: LF = little foam formation, MF = medium foam formation, HF = high foam formation

The results of this dispersion study indicate that combinations of the acrylated PS 556 oligomer (PS-PEODA-76) and either Desonic 9n or Surfynol 104E produce the most stable aqueous dispersions with the commercial acrylated urethane oligomer RSX 89462. The suppression of foam was judged to be an important property in selecting a surfactant system for this UV curing coating. The combination of PS-PEODA-76) and Desonic 9n gave the best level of dispersion and a reasonably short-lived foam. This blend of surfactants was used to prepare samples for the UV curing study.

4.2.2 Viscosity Characteristics of Waterborne UV-Curing Formulations

The viscosities of selected waterborne formulations were measured at different viscometer spindle rotational speeds to study the effect of shear rate on formulation viscosity. Departures for Newtonian viscosity behavior where the viscosity measured is independent of shear rate are frequently desired in coating formulations. Thixotropy or a decrease in viscosity with increasing shear rate is the most frequently encountered rheology in liquid paints. This property allows facile

paint flow at high applied shear rates such as during brushing or spraying but low flow at rest so that sagging is minimized. Some thixotropic tendencies were observed for the experimental waterborne formulations. This behavior is illustrated in the plot of viscosity vs. spindle RPM for several experimental formulations in Figure 4.2.

Effect of Shear Rate on Formulation Viscosity
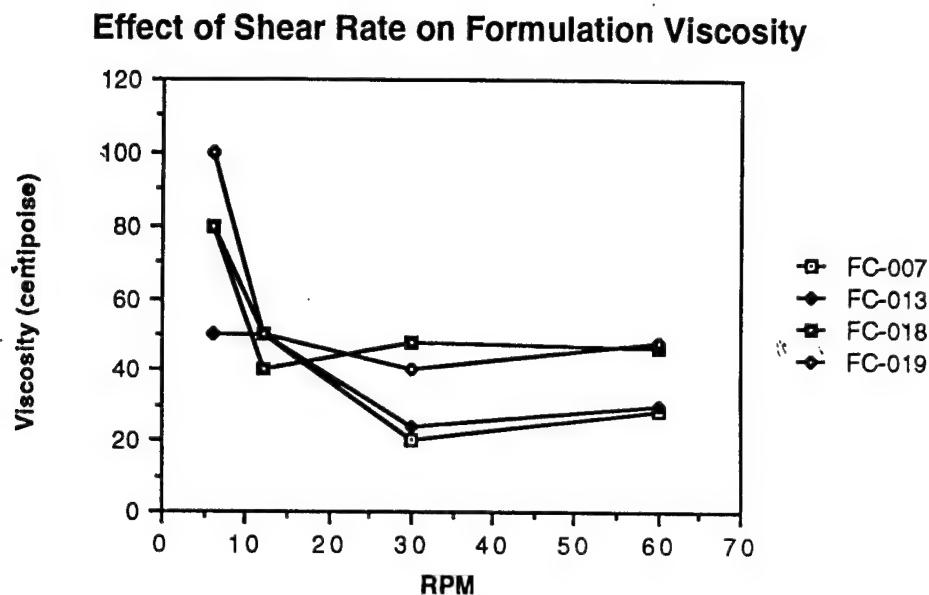
Figure 4.2   Rheological Characteristics of Experimental Waterborne UV Curing Formulations

4.3   Waterborne Coating UV Cure Study

The components of the UV-curable formulations are designed to impart water resistance, flexibility, adhesive qualities and mechanical strength in the cured materials. Figure 4.4 illustrates the chemical structures of the important components of this coating system. The structure of the acrylated polyurethane is not necessarily representative of the commercial product used in this study but is shown as an example of an aliphatic polyurethane with acrylate functionality.

16
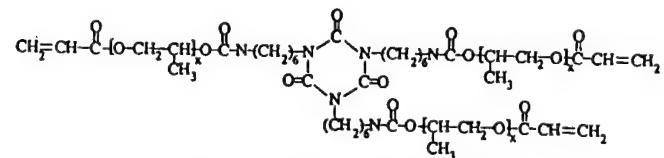
Acrylated Aliphatic Polyurethane Oligomer
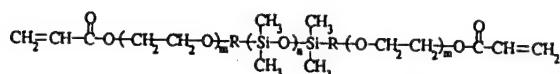
Acrylated Silicone Polyether Oligomer
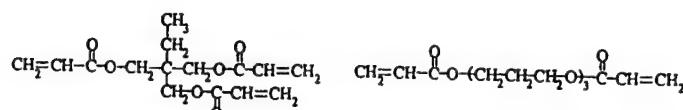
Trimethylolpropane Triacrylate   **Tripropylene Glycol Diacrylate**
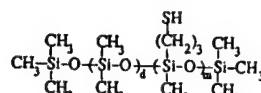
Poly (Mercaptomethyl-co-Dimethyl Siloxane)

Figure 4.3   Chemical Structures of Waterborne Coating Components

4.4 UV Cured Coating Properties

A variety of waterborne coating formulations were prepared and cured into free films or fabric coatings. The water resistance of the films was tested by measuring water drop contact angles and degree of water absorption. The tensile properties of free films and the level of adhesion between coating films and a polyester substrate were determined.

4.4.1 Water Contact Angle

Contact angle measurements are typically performed to obtain information about how liquids wet and potentially interact with solid substrates. The technique has been used to measure the surface tension of a solid [19] and was used here to assess the hydrophobicity of the experimental coatings. The technique, while not necessarily predicting waterproofing efficacy, gives useful information about such phenomena as silicone migration during cure, initial water repellency, and maintenance of water repellency. Since water drop contact angles are dependent on surface wetting, it is assumed that achieving and maintaining the highest possible contact angle would be beneficial in a waterproof coating. This method, however, measures a surface phenomenon and should not be used as an indicator of bulk material properties such as liquid and vapor transmission.

The contact angles of experimental coatings on aluminum foil as well as on fabric substrates with experimental formulations and control waterproofing treatments were measured. In addition, the contact angles of both the air-coating interface and the aluminum-coating interface of several silicone-modified UV-cured samples were measured. The results are shown in the following

17

tables with values measured with other common materials included for comparison.

Table 4.2
Contact Angle Measurements for Water on Different Substrates

Material	Contact Angle (degrees)
Mylar Film (PET)	70
Teflon Film (PTFE)	70
Polyethylene (LLDPE)	90-95
Fabric Coated with DC 61[a]	90

a: Dacron polyester fabric coated with Dow Corning Fabric Coating 61(polydimethylsiloxane)

Table 4.3 lists the water drop contact angles measured on both sides of the coating film. The test samples are arranged in order of increasing silicone content since this appeared to have some bearing on the hydrophobicity of the coatings.

Table 4.3
UV Cured Waterborne Coating Water Repellency Properties

Sample	Siloxane Content	Crosslinker Content	Surfactant Content	Contact Angle (deg) Air Interface	Contact Angle (deg) Substrate Interface
FC-001	5.5	4.5	10.3	37	44
FC-014	11.5	1.9	12.9	32	20
FC-018	15.0	2.0	10.0	90	12
FC-018[a]	15.0	2.0	10.0	95	NA[b]
FC-019	15.0	2.0	10.0	90	90
FC-007	15.6	3.5	12.1	66	70
FC-002	17.2	4.0	8.4	36	29
FC-003	17.2	3.4	10.7	42	38
FC-015	19.0	1.9	9.6	30	58
FC-016	19.0	1.9	9.5	55	10
FC-017	19.0	1.9	9.5	50	15
FC-009	20.0	2.0	16.0	31	59
FC-010	20.0	2.0	12.0	50	50
FC-012	20.4	-----	10.2	61	63
FC-011	20.5	2.0	8.2	69	48
FC-013	20.8	2.1	8.3	42	39
FC-008	22.3	3.0	14.1	67	40

a: Dacron polyester fabric coated with FC-018
b: Not Applicable

The formulations which yielded films having the highest surface hydrophobicity values tended to have 10 percent of less total surfactant content, 15 percent polysiloxane and roughly 2 percent crosslinker. In many cases e.g., samples FC-018 and FC-017, the difference in contact angle between top (air-coating interface) and bottom (coating-substrate interface) surfaces was quite dramatic. In other specimens, however, the differences in contact angle were minimal, e.g., samples FC-019 and FC-012. The mechanism and compositional factors behind this behavior are as yet unclear.

The sample of FC-018 used to coat the polyester fabric had been stored in a tightly capped opaque polyethylene bottle for approximately 2 months before using for this application. The free film had been prepared within hours of its formulation. The water drop contact angles measured for these two specimens were essentially the same as were the overall handling qualities of the liquid formulation after storage.

4.4.2 Water Absorption

The water absorption values of cured free films derived from selected waterborne coating formulations are provided in Table 4.4. The values listed for percent weight gain after soaking for 2 hours represent the average of three specimens and the uncertainty is reported as a standard deviation. The samples are listed in order of increasing level of total surfactants in the formulation.

Table 4.4
UV Cured Waterborne Coating Free Film Water Absorption

Sample	Siloxane Content Weight %	Crosslinker Content Weight %	Surfactant Content Weight %	Photoinitiator Type	Water Absorption (percent)
FC-011	20.5	2.0	8.2	BZME	1.3 ± 0.5
FC-013	20.8	2.1	8.3	BZME	1.0 ± 0.3
FC-015	19.0	1.9	9.6	BZME	0.2 ± 0.2
FC-018	15.0	2.0	10.0	BZME	1.0 ± 0.6
FC-019	15.0	2.0	10.0	BZME	0.2 ± 0.2
FC-012	20.4	-----	10.2	BZME	6 ± 2
FC-001	5.5	4.5	10.3	Irgacure 907	1.5 ± 0.5
FC-003	17.2	3.4	10.7	Irgacure 907	2.9 ± 0.5
FC-010	20.0	2.0	12.0	BZME	1.6 ± 0.5
FC-007	15.6	3.5	12.1	BZME	2 ± 1
FC-014	11.5	1.9	12.9	BZME	1.3 ± 0.3
FC-008	22.3	3.0	14.1	BZME	2.2 ± 0.6
FC-009	20.0	2.0	16.0	BZME	2.3 ± 0.5

The level of surfactants in the coating formulations appeared to be the most important factor in determining the water resistance of UV-cured films. This relationship is illustrated in the bar graph shown in Figure 4.5.

Effect of Surfactant Content on Water Absorption
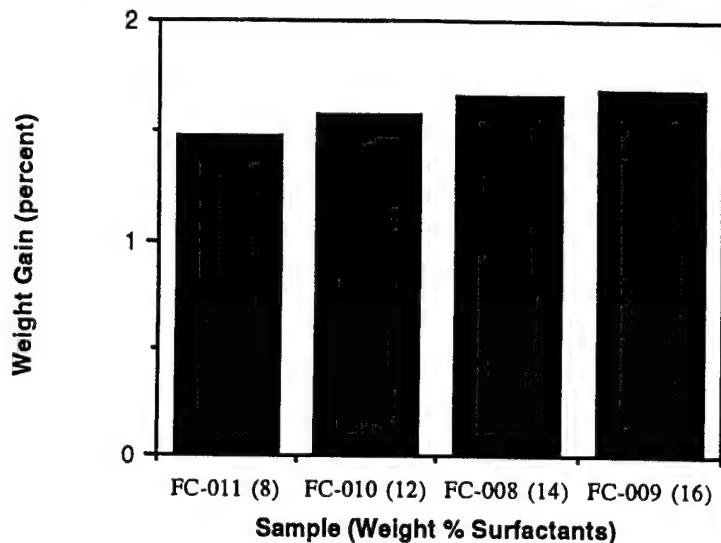
Figure 4.4   Surfactant Level Effects on Cured Coating Water Absorption

In addition to the surfactant level, the crosslink density was also found to have an effect on water absorption. Comparing samples FC-011, FC-009 and FC-012, which have similar levels of silicone and surfactants but differ on the amount of crosslinkers, one can see a dramatic increase in water sensitivity for the FC-012 material. For optimal water absorption resistance, then, it is recommended that: the crosslink density be as high as possible; the total surfactant level, as a percentage of the dry film weight be less than 10 percent; and that the surfactants contain reactive functionality such as acrylic groups to prevent being extracted from the cured coatings.

4.4.3 Free Film Mechanical Properties

The mechanical properties of cured free films of selected waterborne coating formulations are provided in Table 4.5. The values listed for tensile strength and percent elongation represent the average of five specimens and the uncertainty is reported as a standard deviation.

Table 4.5
UV Cured Waterborne Coating Free Film Mechanical Properties

Sample	Siloxane Content Weight %	Crosslinker Content Weight %	Surfactant Content Weight %	Ultimate Tensile Strength (lbs/in^2)	Elongation At Break (percent)
FC-001	5.5	4.5	10.3	440 ± 90	11 ± 4
FC-007	15.6	3.5	12.1	450 ± 70	12 ± 2
FC-008	22.3	3.0	14.1	250 ± 80	7 ± 2
FC-009	20.0	2.0	16.0	270 ± 50	7 ± 1
FC-010	20.0	2.0	12.0	300 ± 50	9 ± 1
FC-011	20.5	2.0	8.2	560 ± 30	8 ± 2
FC-012	20.4	-----	10.2	260 ± 40	9 ± 2
FC-013	20.8	2.1	8.3	400 ± 40	11 ± 2
FC-014	11.5	1.9	12.9	310 ± 70	8 ± 3
FC-018	15.0	2.0	10.0	700 ± 100	13 ± 2
FC-019	15.0	2.0	10.0	400 ± 100	15 ± 2

The development of high tensile strength in these UV-cured films appears to be most dependent on the level of RSX 89462 resin in the formulations. The amount of surfactant also seems to affect the tensile properties, albeit, in an inverse relationship. The samples which exhibited the highest tensile strength had surfactant contents of 10 weight percent of solids or less. The elongation at break measured for these specimens appeared to coincide with the tensile strength, i.e., the samples with the higher breaking strengths also had the highest ultimate elongation. A load-elongation curve for one of the specimens from the FC-011 sample set is shown in Figure 4.6. The slightly S-shaped form of the trace suggests a highly crosslinked elastomeric solid. While the coating samples tested in this study appear to have more than adequate tensile strength, their flexibility, as measured by elongation at break, are probably too low for this application. The flexibility of crosslinked polymers such as these is inversely related to the crosslink density. In order to improve the extensibility of the resins employed for these coatings, the total crosslinker level would have to be decreased. Replacement of the polyfunctional acrylic crosslinkers such as TMPTA would be the preferred since these compounds are presumed to be the ingredients of most toxicological concern in the formulation. Other ways of reducing the crosslink density and/or increasing the flexibility of the cured resins would include: using silicone copolymers with lower mercaptopropyl content, using higher molecular weight urethane diacrylate oligomers, using urethane diacrylates with higher levels of soft block components and/or more flexible soft blocks, and using higher molecular weight diacrylate crosslinkers.
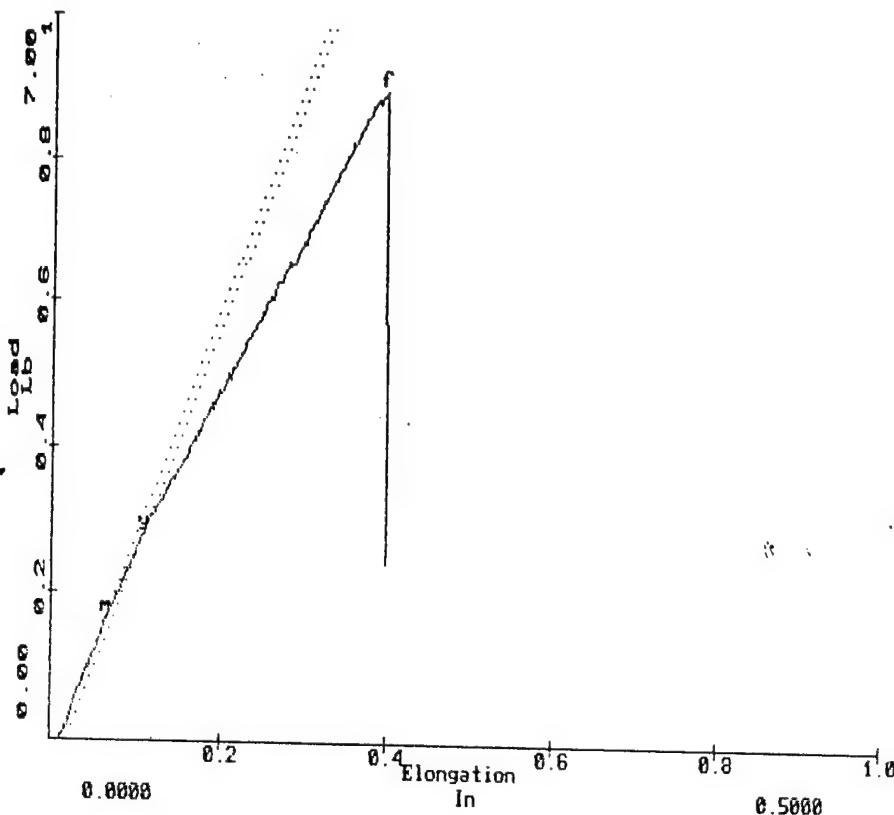
Figure 4.5   Load-Elongation Curve for UV-Cured Film Derived from FC-011

4.4.4 Coating-to-Fabric Adhesion

Several coated fabrics were tested for coating-to-fabric adhesion by a direct (90 degree) pull-off mechanical method. A Dacron polyester sailcloth fabric was used as the substrate for FC-011, FC-019 and Dow Corning Fabric Coating 61. A five minute epoxy adhesive (Devcon Corp.) was used to adhere the coated fabric samples to the smaller diameter aluminum test die and larger aluminum cylinder. For the samples coated with commercial DC Fabric Coating 61 and the fabric sample coated with FC-011, the mode of adhesive failure was between the coating surface and the adhesive itself. No waterproof coating was removed from these specimens so the values listed in Table 4.6 only represent a minimum coating-to-fabric adhesion level. This unintended mode of failure was also observed in 2 of the 3 samples prepared with experimental coating FC-019. In one case though, roughly half of the coating was removed in the test and the average strength measured was approximately 500 psi. Since the tensile strength measured for this coating sample was roughly equal to this adhesive strength, the coating-to-fabric adhesion would be considered excellent. How this adhesion level would compare to commercial waterproof fabric coatings would depend on the mechanical properties of the of coating binder, the fabric substrate, the method of coating, and the method of testing. For example, the DC Fabric Coating 60 has a reported free-film tensile strength of 400 psi.[8] Therefore, its maximum adhesive strength would not be expected to exceed this level.

22

Table 4.6
Coating-to Fabric Adhesion

Material	Adhesive Strength (psi)
D C Fabric Coating 61	60
FC-011	90
FC-019	500

5.0 CONCLUSIONS

This Phase I research program has demonstrated the feasibility of preparing a low-VOC, one-component, waterborne silicone-modified polyurethane coating for waterproofing fabrics. These formulations yield flexible, adherent coatings to fabrics, resist water penetration effectively and, in the uncured state, comply with present EPA regulations.

Specifically, the feasibility research resulted in the following accomplishments:

- It was demonstrated that acrylated poly(siloxane-ether) copolymers could be synthesized, dispersed in water, and crosslinked by a UV photoinitiation process.

- That acrylated poly(siloxane-ether) copolymers in combination with nonylphenol ethoxylate surfactants serve as effective emulsifiers for commercial aliphatic polyurethane-based acrylated oligomers.

- That waterborne coating formulations based on commercial acrylated aliphatic polyurethane oligomers, mercaptyl-functional polysiloxane, acrylic crosslinkers, and photoinitiators could be readily cured by UV irradiation into tough, water resistant films.

- That solvent-free waterborne coating formulations could be prepared and cured into uniform and cohesive films.

- That selected waterborne coating formulations yielded films having extremely hydrophobic top surfaces for water repellency and hydrophilic bottom surfaces for adhesion to fabric substrates.

- That the degree of water absorption, water repellency, and mechanical strength can be controlled through compositional variations.

- That single component formulations based on this technology have good shelf stability for a minimum of two months when protected from light.

- That UV cured coatings appear to adhere strongly to typical fabrics such as polyester and possess surfaces that resist adhesion to epoxy adhesives.

6.0 RECOMMENDATIONS

The main technical goal of this research program was to demonstrate the feasibility of using new UV-curable silicone polyether surfactants to prepare waterborne coating products for rendering clothing and fabric articles waterproof. An effective coating system was developed which is water-reducible, employs no organic solvents, produces cured coatings having high water repellency, low water absorption, flexibility and excellent adhesion to fabrics. A review of the main coating technologies currently available having applicability in fabric waterproofing revealed that UV-curing and water-reducible formulation remain the best alternatives to current solvent and plasticizer-based coating methods. Recommendations for additional research in the area of UV-curing waterborne coatings would include:

- A systematic developmental study for optimizing the waterborne UV-curing fabric coating system including statistical experimental design, e. g., Taguchi method
- Investigate supercritical CO_2 as a formulation diluent for UV-curing coating applications

- Determine and evaluate factors governing other properties in waterproof wearing apparel:

   fabric feel (comfort), drapability, and water vapor permeability
   coating colorability and pigmentation
   durability , e. g. resistance to repeated laundering cycles
   resistance to other contaminants, e. g., oil, gasoline, CWAs, soil
   weatherability, e. g., temperature extremes, UV light, oxidation

- Manufacturing issues:

   Material costs for coating formulator
   Material costs for coating end user
   Equipment and labor requirements
   Worker health and safety
   Disposal costs

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APPENDICES

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APPENDIX A

FTIR Spectra

PERKIN ELMER

126.95
%T

36.07
CURSOR
1725.0
cm⁻¹

8.20

4000 3500 3000 2500 2000 1500 1000 cm⁻¹ 500

1725.0
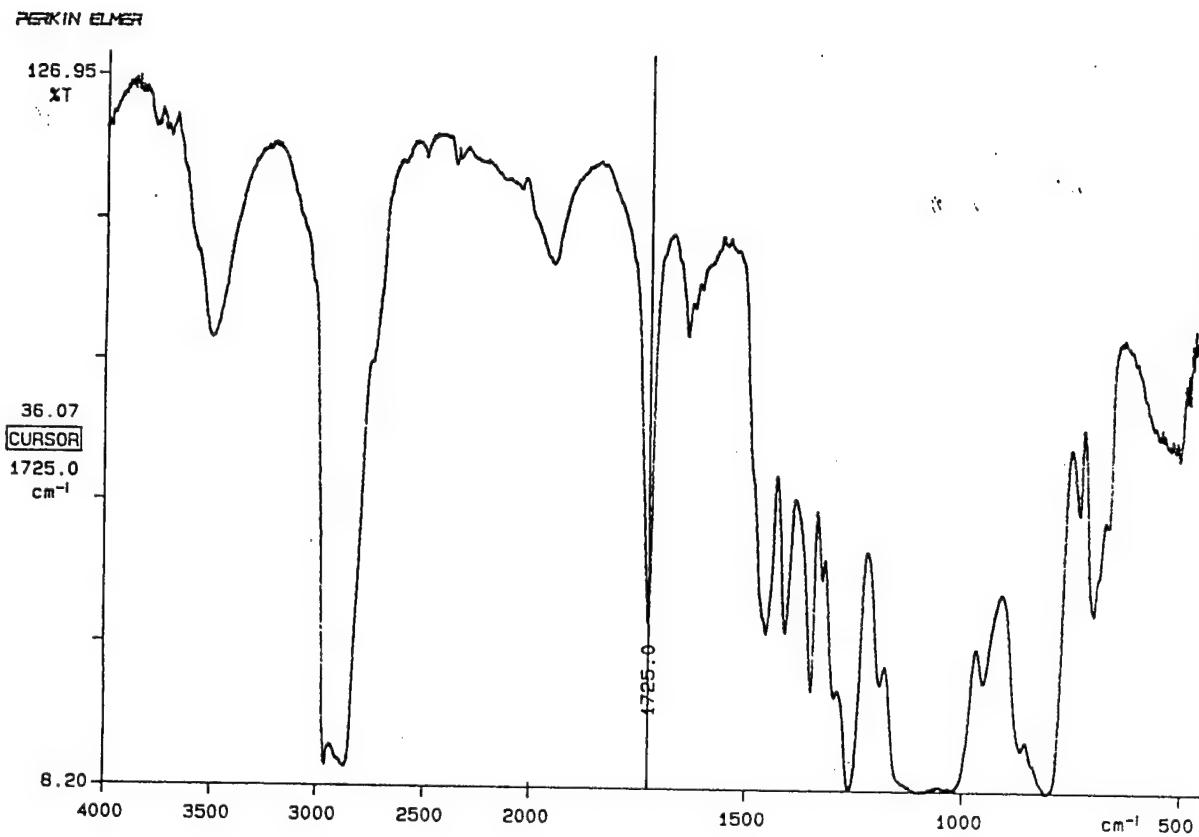
93/06/03 10: 34 Cape Cod Research
ps555da: 4 scans, 4.0cm-1
ps555da pure product

Figure A-1   FTIR (transmission) Spectrum of Acrylated PS 555 (PS-PEODA-50)
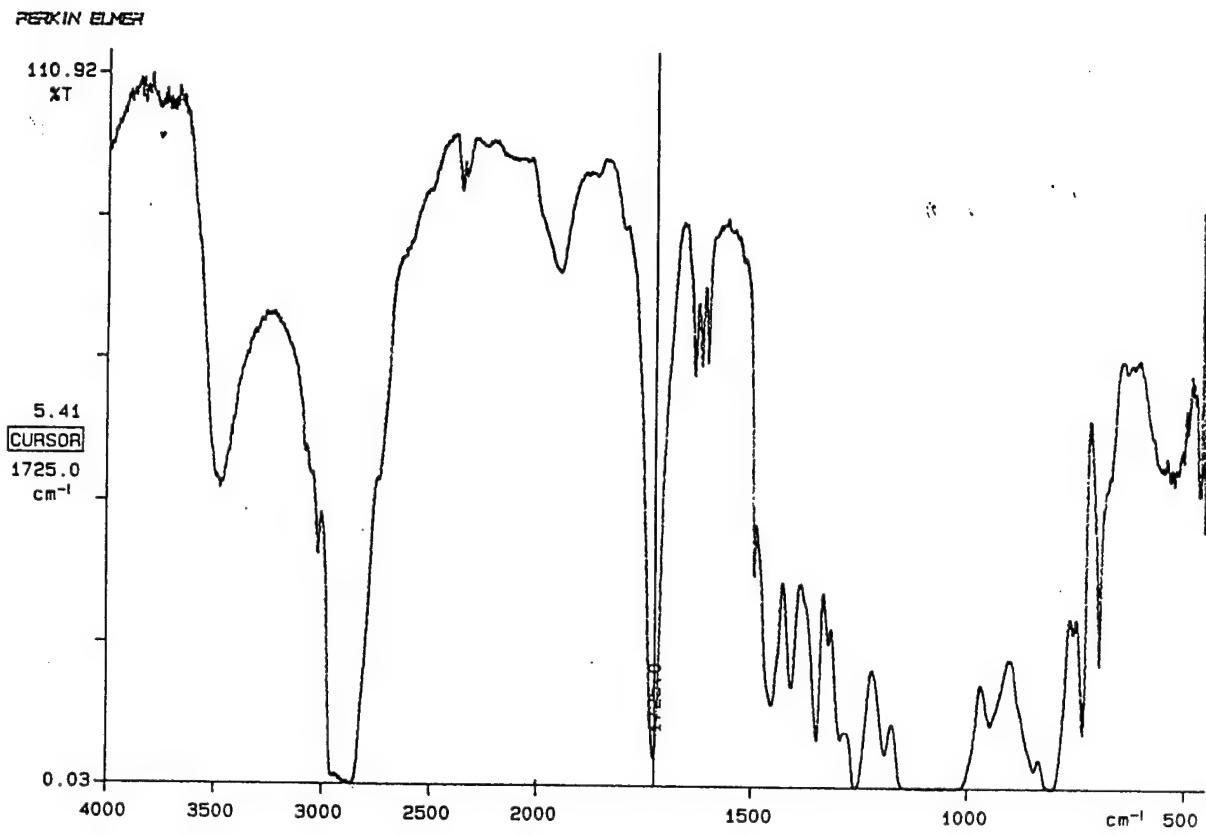
32

Figure A-2   FTIR (transmission) Spectrum of Acrylated PS 556 (PS-PEODA-76)

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APPENDIX B

Experimental Details of UV-Curable Emulsifier Synthesis

Materials

PS 555: Carbinol Terminated, Polydimethyl siloxane resin, 50 % ethylene oxide content, 1100-1300 g/ hydroxyl eqiv., Huels America, Inc.
PS-556: Carbinol Terminated, Polydimethyl siloxane resin, 76 % ethylene oxide content, 500-750 g/ hydroxyl eqiv., Huels America, Inc.
Acryloyl Chloride, 98%, Aldrich Chem. Co.
Reillex 425 beads (crosslinked poly(vinyl pyridine), Reilly Industries, Inc.)

Procedure for Synthesizing Acrylated Surfactants

Into a 100'ml, three-necked round bottom flask fitted with a Dean-Stark trap, water-cooled West condenser with nitrogen gas inlet, pressure equilizing addition funnel, and magnetic stir bar was charged: 15.182 g of PS 556, 4.968g of pre-dried Reillex 425 beads, and 30 .0 ml of reagent grade toluene. The mixture was stirred and warmed by means of a silicone oil bath and magnetic stirrer hot plate to the reflux temperature of toluene (ca 130 °C). Approximately 15 ml of toluene was distilled into the Dean-Stark trap and removed to dry the system. The reaction mixture temperature was lowered to 80 °C and 2.40 g (26 54 mmole) of acryloyl chloride was added dropwise to the mixture over the course of 30 minutes. The temperature was maintained at 80 °C and the mixture was stirred under a nitrogen purge for 20 hours. The product mixture was analyzed by FTIR and revealed a peak at 1725 cm $^{-1}$ corresponding to ester functionality. The reaction mixture was cooled and filtered under reduced pressure to remove the Reillex beads. The resulting clear solution was vacuum stripped by elevated temperature rotary evaporation at which time a gellation took place. The gel was dissolved in acetone and vacuum stripped to yield a clear, slightly yellow-tinted fluid.

APPENDIX C

Waterborne UV-Curable Coating Formulations

Table C-1
UV Coating Materials

Acrylated Oligomers
Genomer D1200PD, acrylated aliphatic polyurethane, (Hans Rahn & Co.)
Ebecryl 6700, acrylated aromatic urethane oligomer (UCB Radcure, Inc.)
RSX 89462, acrylated aliphatic polyurethane oligomer, (UCB Radcure, Inc.)
Ebecryl 230, acrylated aliphatic polyurethane oligomer, (UCB Radcure, Inc.)

UV Crosslinkers
TMPTA, Trimethylolpropane triacrylate, (Aldrich Chem. Co.)
TRPGDA, Tripropylene glycol diacrylate, (Aldrich Chem. Co.)
PS 850.5   poly(dimethyl-co-mercaptopropylmethyl) siloxane, 14 mole% mercaptopropyl-
             methyl groups (Huels America Corp.)
PS 849   poly(dimethyl-co-mercaptopropylmethyl) siloxane, 2 mole% mercaptopropyl-
             methyl groups (Huels America Corp.)

UV Initiators
Irgacure 907, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone, (Ciba-Geigy Corp.)
Irgacure 369, (2-benzyl-2-N, N-Dimethylamino-1-(4-morpholinophenyl)-butanone, (Ciba-Geigy
             Corp.)
Benzoin Methyl Ether,   (Aldrich Chemical Co.)

Coalescing Solvents
PGMEA   propylene glycol methylether acetate, reagent grade, (Aldrich Chem. Co.)
PGME   1-methoxy-2-propanol, 98%, (Aldrich Chem. Co.)

Surfactants
PS-PEODA-76   Acrylate-terminated poly(dimethylsiloxane-co-ethylene oxide) resin, 76
               % ethylene oxide content.
PS-PEODA-50   Acrylate-terminated poly(dimethylsiloxane-co-ethylene oxide) resin, 50
               % ethylene oxide content.
Hamposyl L-95 Sodium lauroyl sarcosinate, 95 % (W. R. Grace & Co.)
Hamposyl O   Oleoyl sarcosine, 94 % (W. R. Grace & Co.)
Surfynol 104E Tertiary acetylenic diol (50 % by weight in ethylene glycol), (Air
               Products and Chemicals, Inc.)
Span 80   Sorbitan monooleate, ICI Chemicals, Inc.
Brij-30   Polyoxyethylene(4) lauryl ether, (Aldrich Chemical Co.)
Desonic 9N   Nonyl phenol polyethoxylate (Desoto Chem. Corp.)

Thickeners
Hydrophobic Fumed Silica   (Cab-O-Sil TS-720, Cabot Corp.)

Irgacure photoinitiators were generously supplied by the Ciba-Geigy Corporation. Ebecryl and
RSX acrylated oligomers were generously provided by the UCB Radcure Corporation, and
Genomer D1200PD was generously supplied by the Biddle Sawyer Corporation.

Table C-2
RSX 89462 UV Curing Study Formulations

FC001

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.139	77.42	41.45
TMPTA	0.576	4.40	2.35
Desonic 9N	0.674	5.15	2.76
PEODA-56	0.674	5.15	2.76
PS 849	0.725	5.54	2.96
Irgacure 907	0.306	2.34	1.25
Water	11.369	------	46.47

FC002

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.121	68.29	38.82
TMPTA	0.600	4.05	2.30
Desonic 9N	0.462	3.12	1.77
PEODA-56	0.781	5.27	3.00
PS 849	2.554	17.23	9.80
Irgacure 907	0.302	2.04	1.16
Water	11.249	------	43.15

FC003

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.008	66.65	38.34
TMPTA	0.510	3.40	1.95
Desonic 9N	0.806	5.37	3.09
PEODA-56	0.799	5.32	3.06
PS 849	1.288	8.58	4.93
PS 850.5	1.299	8.65	4.98
BZME	------	------	------
Irgacure 907	0.306	2.04	1.17
Water	11.089	------	42.48

FC007

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.028	66.71	38.70
TMPTA	0.525	3.49	2.03
Desonic 9N	0.911	6.06	3.52
PEODA-56	0.902	6.00	3.48
PS 849	2.353	15.65	9.08
PS 850.5	------	------	------
BZME	0.314	2.09	1.21
Irgacure 907	------	------	------
Water	10.878	------	41.98

39

FC008

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.024	58.78	53.92
TMPTA	0.515	3.02	1.84
Desonic 9N	1.204	7.06	4.31
PEODA-56	1.204	7.06	4.31
PS 849	3.804	22.31	13.63
BZME	0.302	1.77	1.08
Water	10.854	------	38.89

FC009

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.029	60.00	36.00
TMPTA	0.334	2.00	1.20
Desonic 9N	1.337	8.00	4.80
PEODA-56	1.337	8.00	4.80
PS 849	3.343	20.00	12.00
BZME	0.334	2.00	1.20
Water	11.145	------	40.00

FC010

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.864	63.97	37.96
TMPTA	0.340	2.00	1.19
Desonic 9N	1.020	6.01	3.56
PEODA-56	1.020	6.01	3.56
PS 849	3.400	20.02	11.88
BZME	0.340	2.00	1.19
Water	11.632	------	40.65

FC011

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.179	67.25	38.48
TMPTA	0.308	2.04	1.16
Desonic 9N	0.620	4.10	2.24
PEODA-56	0.620	4.10	2.34
PS 849	3.100	20.48	11.72
BZME	0.308	2.04	1.16
Water	11.321	------	42.79

FC012

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.862	67.33	40.81
TRPGDA	-------	-------	-------
Desonic 9N	0.843	5.23	3.17
PEODA-56	0.806	5.00	3.03
PS 849	3.286	20.37	12.35
BZME	0.335	2.08	1.26
Water	10.483	------	39.39

FC013

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.206	66.58	38.78
TRPGDA	0.327	2.13	1.24
Desonic 9N	0.638	4.16	2.42
PEODA-56	0.638	4.16	2.42
PS 849	3.194	20.83	12.14
BZME	0.327	2.13	1.24
Water	10.987	------	41.75

FC014

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.243	58.05	36.49
TMPTA	0.335	1.90	1.19
Desonic 9N	1.138	6.45	4.05
PEODA-56	1.138	6.45	4.05
PS 849	3.240	11.54	11.22
BZME	0.649	3.68	2.31
Fumed Silica	0.901	5.11	3.21
Water	10.426	------	37.14

FC015

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.006	66.66	40.71
TMPTA	0.286	1.91	1.16
Desonic 9N	0.716	4.77	1.74
PEODA-56	0.716	4.77	1.74
PS 849	2.858	19.04	11.63
BZME	0.429	2.86	1.74
Fumed Silica	------	------	------
Water	9.568	------	38.93

41

FC016

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.064	66.67	39.11
TMPTA	------	------	------
TRPGDA	0.288	1.91	1.12
Desonic 9N	0.719	4.76	2.79
PEODA-56	0.719	4.76	2.79
PS 849	2.875	19.04	11.17
BZME	0.431	2.86	1.68
Water	10.633	------	41.33

FC017

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.076	66.68	39.24
TMPTA	0.144	0.95	0.56
TRPGDA	0.144	0.95	0.56
Desonic 9N	0.719	4.76	2.80
PEODA-56	0.719	4.76	2.80
PS 849	2.878	19.04	11.21
BZME	0.432	2.86	1.68
Water	10.564	------	41.14

FC018

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.000	70.01	42.00
TMPTA	0.286	2.00	1.20
TRPGDA	------	------	------
Desonic 9N	0.714	5.00	3.00
PEODA-56	0.714	5.00	3.00
PS 849	2.140	14.98	8.99
BZME	0.429	3.00	1.80
Water	9.523	------	40.00

FC019

Material	Wt.(g)	Wt.(%) Solids	Wt.(%) Total
RSX 89462	10.180	70.01	41.99
TMPTA	------	------	------
TRPGDA	0.291	2.00	1.20
Desonic 9N	0.727	5.00	3.00
PEODA-56	0.727	5.00	3.00
PS 849	2.180	14.99	8.99
BZME	0.436	3.00	2.40
Water	9.701	------	40.02